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A Novel Method of Removing Impurities from Multilevel Interconnect Materials

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A novel method of removing impurities from dielectric films has been developed. The removal of water and charges is accomplished by humidification and wet pretreatment followed by charge extraction with CO_2 supercritical fluid (SCF). Films treated in this manner exhibit intrinsic properties, which are usually masked by moisture and impurities.
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KEYWORDS: supercritical, CO_2, low-*k*, dehydration, impurity removal, leakage current, *I–V* characteristics, *C–V* characteristics

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1. Introduction

We have been investigating novel interlayer dielectric (ILD) processes using new materials. As is well known, low-*k* films with a k of less than 2.5 exhibit a large leakage current.[1,2] In the determination of the intrinsic properties of materials and the assessment their applicability to ILDs, a new method of removing impurities is indispensable because impurities degrade the electrical characteristics and mask the intrinsic properties. Figure 1 shows the *I–E* characteristics of a representative conventional porous film. The leakage current increases gradually with temperature and at temperatures greater than 90°C, the current is too large to measure. Considering that a large leakage current might be caused by impurities such as moisture and charges in the film, we carried out experiments using Supercritical Fluid (SCF) consisting of CO_2.

CO_2 SCF is widely used for the impurity extraction, dehydration and drying of materials with a fine structure.[3,4] Our aim is to use SCF to remove impurities from ILDs, as illustrated in Fig. 2. This involves two processes: dehydration and charge removal. Our basic concept is that, if H_2O is moved in close proximity to the charges in the film by pretreatment, the charges will be removed along with H_2O by subsequent CO_2 SCF treatment.

2. Basic Experimental Conditions

Films were deposited on 8 inch wafers, and treated with CO_2 SCF at a temperature of 80°C and a pressure of 15 Mpa[3] to remove moisture and impurities from films.

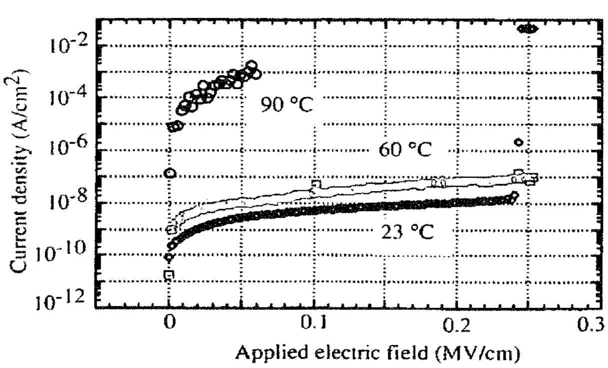

Fig. 1. *I–E* characteristics of representative porous film.

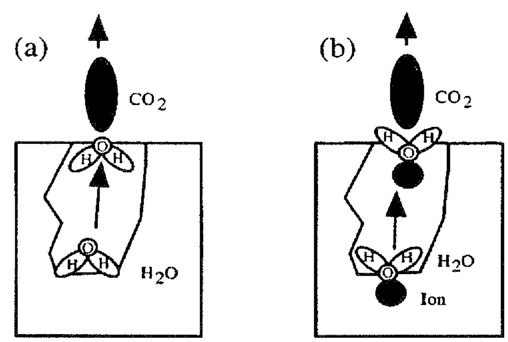

Fig. 2. Schematic of (a) dehydration and (b) charge removal.

Pretreatments included dipping and boiling in DI water to remove any charges. SCF CO_2 treatment times of 2, 10, 30 and 60 min were used, although the typical time was 30 min. Samples were dipped in DI water for 1 h or boiled for the same period. Thermal desorption spectra (TDS) were obtained using a conventional system, and samples were preheated for 10 min before measurements. The amount of impurities in films immersed in NaOH solution was measured by conventional SIMS. In this experiment, chipped samples were used.

The electrical, that is, the *I–V* (*E*) and *C–V*, characteristics were measured using an MIS structure with Al dots 1 mm in diameter. The *I–V* (*E*) characteristics were measured at temperatures from 23°C to 150°C, and the *C–V* characteristics were measured at 23°C. The leakage current between adjacent interconnects was measured using a sample with one pair of comb patterns (linewidth: 0.24 µm; spacing: 0.24 µm; height: 0.4 µm). The materials evaluated were P-TEOS (TEOS deposited by plasma CVD), porous organic SOG, parylene fluoride, and polyphenylene.

The samples were conveyed in a vacuum desiccator as soon as possible to the electrode deposition step or to the next step after CO_2 SCF treatment. The electrical characteristics were measured using a vacuum prober described in ref. 5. The experimental procedure for this study is illustrated in Fig. 3.

3. Results and Discussion

3.1 *Precheck of CO_2 SCF treatment using P-TEOS film*

First, we assessed the effectiveness of CO_2 SCF on P-TEOS films. Figure 4 shows a comparison of the TDS of a conventional P-TEOS film and a film treated with CO_2 SCF.

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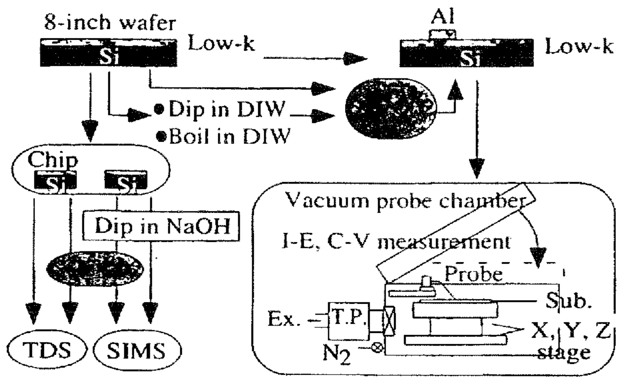

Fig. 3. Experimental procedure.

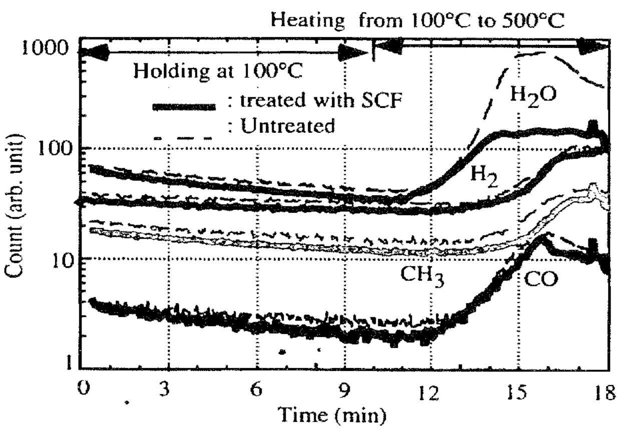

Fig. 4. TDS of untreated P-TEOS film and film treated with CO_2 SCF.

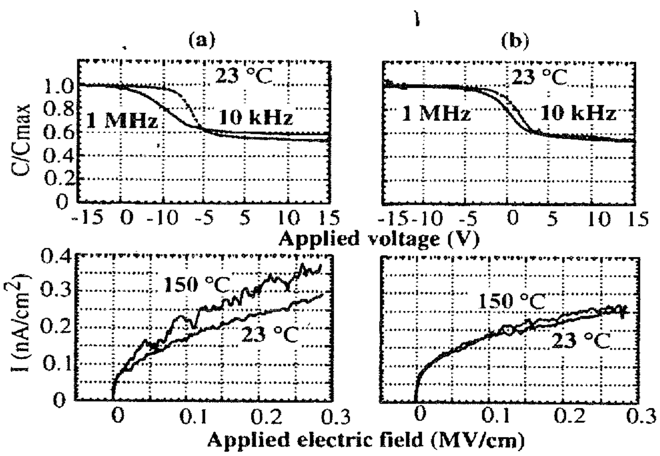

Fig. 5. *C–V* and *I–E* characteristics of (a) untreated P-TEOS film and (b) film treated with CO_2 SCF.

Although representative signals for H_2, O_2, and CH_3 have the same strengths for both films, the signal strength of H_2O for the treated film is only half that for the untreated film. Figure 5 shows the *C–V* and *I–E* characteristics of the films. The Vfb at 1 MHz reflects the net charge of a film, and the difference between the Vfb values at 1 MHz and 10 kHz

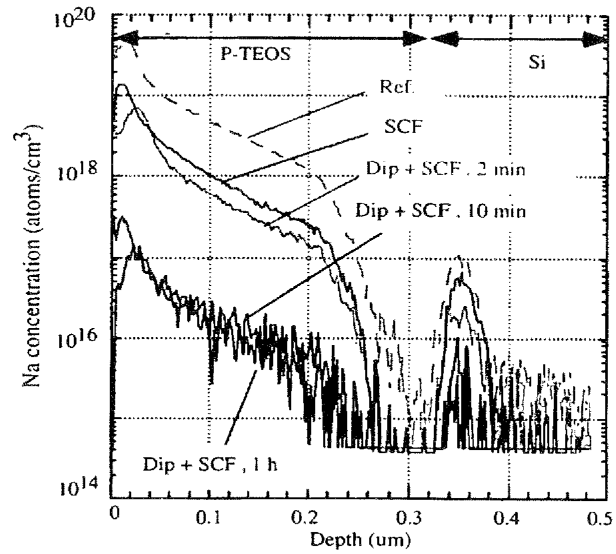

Fig. 6. Depth profiles of Na in P-TEOS films immersed in NaOH solution.

reflects the amount of mobile ions in a film.[1,2] The *C–V* characteristics show that the conventional P-TEOS film contains more positive charges and more mobile positive charges than the treated film. Since the conventional film has more mobile charges than the treated film, the *I–V* characteristics of the conventional film exhibit a larger leakage current at high temperatures. This indicates that CO_2 SCF treatment dehydrates a film and removes mobile charges. Thus, we attempted to remove the charges added to a film by immersing it in NaOH solution.

Figure 6 shows depth profiles of Na in P-TEOS films immersed in 0.01 N NaOH solution for 24 hs. "Ref" indicates a film that was rinsed in DI water and dried in air, and "SCF" indicates a film treated with CO_2 SCF after rinsing and drying. The other curves are for films that were rinsed in DI water and left wet before treatment with CO_2 SCF for 10 min or 1 h. The reference sample has a high concentration of Na. Although only CO_2 SCF treatment, that is, the dehydration treatment, reduces the concentration, the reduction is smaller for films subjected to wet pretreatment. The results show that the amount of Na in these samples decreases as the CO_2 SCF treatment time increases. In addition, it is clear that a sufficient amount of CO_2 SCF penetrates the P-TEOS film to a depth of approximately half a micron when the treatment time is 10 min or more. This demonstrates that treating a wet film with SCF is an effective method of removing charged impurities from a film.

3.2 *Application to porous film*

Figure 7 shows the *I–E* characteristics obtained after the SCF treatment of the same porous film used for the data in Fig. 1. Note that it was possible to measure the characteristics of the treated film at a temperature of 150°C. In contrast, those of the untreated film could not be measured at temperatures above 100°C; thus the curve for 90°C is shown in the figure. SCF treatment is very effective in reducing the leakage current, or, in improving the film properties. This reduction indicates that the large leakage current of the

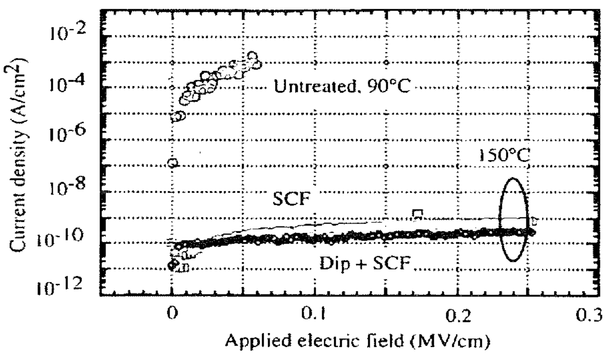

Fig. 7. I–E characteristics of porous film.

conventional film is caused by the moisture in the film. Moreover, SCF treatment in combination with wet pretreatment (dipping in DI water) further reduces the current. This indicates that "dip + SCF" treatment removes the charges from the film.

3.3 Application to low-k organic film

Parylene fluoride is a candidate for a low-k material. Figure 8 shows the I–E and C–V characteristics of the film. Here "boil + SCF" indicates films treated with SCF after being boiled in DI water for 1 h. "2 × (boil + SCF)" indicates film subjected to "boil + SCF" treatment twice. SCF treatment without pretreatment does not seem to have any effect on the film because it does not improve the I–E characteristics. This indicates that dehydration does not influence the properties of this film. Although the degree of improvement is small, pretreatment with DI water dipping shows some effect. This suggests that humidification is very important in the removal of impurities from such organic films. Boiling the sample was also attempted, and proved to be very effective in improving the properties such that it was possible to measure the C–V characteristics. The Vfb of the C–V characteristics reflects the total net charge in a film,[1,2,6] with a negative value indicating that the film contains negative charges. Double "boil + SCF" treatment resulted in further improvement, reducing the leakage current to less than 1×10^{-8} A/cm^2 and making Vfb closer to 0 V. This demonstrates that the intrinsic properties of this low-k film exhibit good dielectric characteristics. This could never have been discovered unless the charges had been removed by humidification and subsequent charge extraction with SCF CO_2.

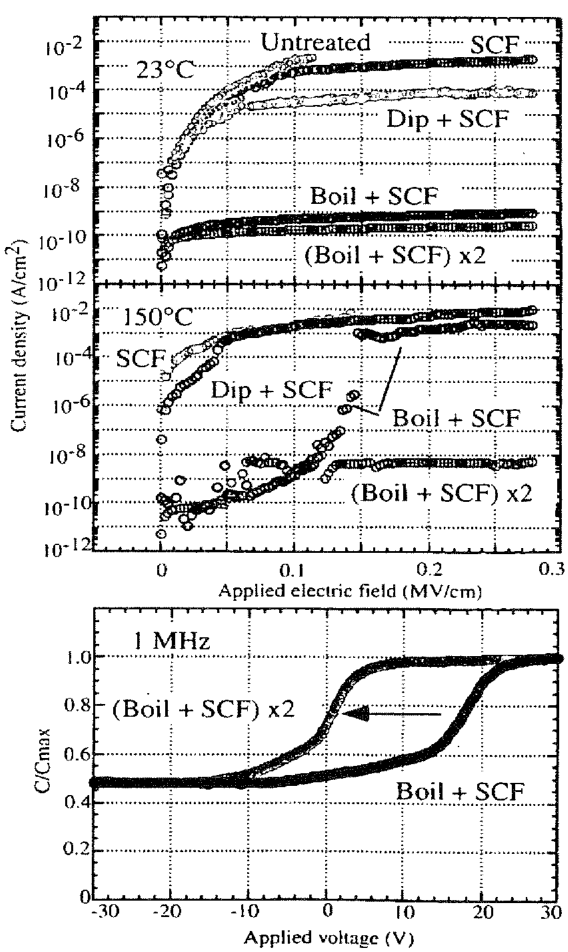

Fig. 8. I–E and C–V characteristics of parylene fluoride film.

3.4 Application to interconnect integration

This removal method can be applied to ILDs after the formation of the interconnect structure. Even common commercially available films often exhibit a large leakage current due to the ILD process used or to small variations in process parameters, such as the annealing temperature. Figure 9 shows the results of applying the method to a conventional film formed under unsuitable conditions. The untreated film exhibits a large leakage current at high temperatures. In contrast, the film subjected to "dip + SCF" treatment after metal line formation has a small leakage current. The current at 150°C has about the same value as that at 30°C. Thus, it is clear that this method of humidification and subsequent charge extraction is very effective in recovering the intrinsic properties of an ILD, even after interconnect formation.

4. Conclusions

We have developed a new treatment method employing supercritical CO_2 that removes impurities from an ILD. We found that the treatment dehydrates an ILD, and that the

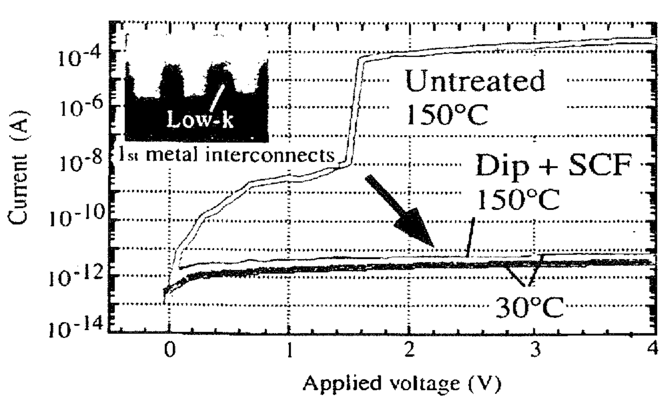

Fig. 9. I–V characteristics of conventional low-k film.

removal of moisture reduces the leakage current. The treatment also removes charges, which markedly improves the electrical characteristics. In fact, this treatment can restore the intrinsic properties of an ILD. Thus, CO_2 SCF treatment is very useful for investigating the nature of ILDs.

Acknowledgments

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1) T. Fukuda, H. Nishino and H. Yanazawa: 201st Meeting of ECS Abstract No. 357 (2002).
2) T. Fukuda, H. Nishino and H. Yanazawa: to be published in Jpn. J. Appl. Phys.
3) K. Suzuki, T. Fujikawa and N. Kawakami: 2000 IITC Proceedings, 2000, p. 105.
4) H. Namatsu, K. Yamazai and K. Kurihara: J. Vac. Sci Technol. B **18** (2000) 780.
5) T. Fukuda, H. Nishino and H. Matsunaga: Jpn. J. Appl. Phys. **41** (2002) L537.
6) S. M. Sze: *Physics of Semiconductor Devices* (John Wiley & Sons, New York, 1981).